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Ozone promoting organic nitrogen change to inorganic in anaerobic livestock wastewater

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ABSTRACT

Ozone aeration may significantly change nitrogen form and availability in anaerobic swine wastewater, hence it is important to characterize the effect of ozone on nitrogen. In order to study the influences of ozone and aeration time on the nitrogen transformation and availability in anaerobic swine wastewater, an indoor experiment was conducted with self-designed ozone producer apparatus under five different durations of ozone aeration, 0, 10, 20, 40 and 60 min, respectively. Water samples were collected in different aeration time and different nitrogen forms were determined. The results showed that different durations of ozone aeration remarkably affected nitrogen contents and formations in wastewater system. Specifically, the content of total nitrogen, soluble Kjeldahl nitrogen, ammonium nitrogen, nitrite nitrogen and particulate organic nitrogen (PON) significantly declined by 10.11%, 6.75%, 17.90%, 98.81% and 89.33% ($p < 0.05$), respectively. On the contrary, the content of nitrate nitrogen and dissolved organic nitrogen increased by 613.85% and 459.85% at the end of 60 min ($p < 0.05$), respectively. The results suggested nitrogen form transformation and nutrient concentration change should be taken into consideration before reusing swine wastewater in irrigation.

Keywords: Ozone; Livestock; Wastewater; Nitrogen; Form

1. Introduction

During the recent years in China, livestock breeding is developing quickly and more professionally; intensification and industrialization, which also generates huge amount of manure and wastewater. Usually, solid manure is collected easily and made of organic fertilizer as plant nutrients. Compared with solid manure, livestock wastewater usually is restored and subjected to anaerobic treatment, but part of the wastewater remains untreated, which seriously restrains the health of livestock and sustainable development. Due to high organic pollutant load in wastewater, as well as a large number of pathogenic microorganisms [1], direct discharge is bound to cause serious pollution of water, air, and endanger human and livestock health [2]. Anaerobic digestion and then reuse to farmland as fertilizer is the best way to treat livestock wastewater nowadays in China [3]. However, pathogenic microorganisms and parasites eggs cannot be removed only by anaerobic treatment. It may also be a potential hazard to plants health when used, especially if it is reused in vegetable production, it may endanger human beings' health [4]. Thus, anaerobic treatment of wastewater

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needs to be sterilized before it is applied to farmland. Ozone aeration is a widely used method which has good disinfection effect [5]. Ozone would decompose the bacterial cell wall and quickly spreads into the cell, militate activity of bacteria and viruses. With the cell and ribonucleic acid destroyed, decomposition of deoxyribonucleic acid, proteins, lipids, polysaccharides and other macromolecular polymers, metabolism and reproduction of bacteria were destructed [6]. In addition, ozone aeration produces less harmful byproducts, and it can also reduce COD, turbidity, chroma [7] in the wastewater. Therefore, it is considered as an environmental friendly fungicide, and better than chlorine, chlorine dioxide and other sterilization preparation [8]. Nevertheless, ozone aeration process will change the nutrient forms thereby affecting nutrient use efficiency, moreover having impact on farmland corps irrigated with the wastewater. In this study, self-design ozone aeration device was applied to treat the pig farm anaerobic wastewater. The purpose is to discuss the effect characteristics of ozone aeration time on nitrogen forms and content in swine wastewater, and to provide a theoretical basis and technical support for the follow-up agricultural efficient use.

2. Materials and methods

2.1. Experimental material

Swine wastewater used in this study was sampled from anaerobic digester from the Tianjin Yililai Breeding Farm Ltd. The main water treatment processes include solid/liquid separation, filtration and homogenization, anaerobic digestion, etc. Anaerobic digester tank with 100 m^3 had a 20 m^3/d wastewater treatment capacity, and the hydraulic retention time was 5 d. The quality of wastewater after anaerobic digestion is shown in Table 1.

2.2. Ozone aeration device

Ozone aeration device used in this study is shown in Fig. 1. Fiber reinforced plastic material was processed to cylinder with a diameter of 12 and 50 cm high. The aeration flowing rate was 3–3.5 L/min with an ozone concentration of 38–60 mg/L. 20 g/L of boric acid was used as ammonia absorption solution. Ozone end gas was absorbed by KI solution with a small amount of soluble starch. Oxygen as raw material for producing ozone was separated from air component by a gas filter at normal temperature and pressure. High-voltage discharger worked to make high-tension current and high-voltage corona field, which could promote oxygen molecules in inner or surrounding field conversing into ozone molecules by electrochemical reaction.

Table 1
Quality of wastewater after anaerobic digestion

TKN (mg·L^{-1})	806.34
DKN (mg·L^{-1})	721.64
NH_4-N (mg·L^{-1})	704.53
NO_3-N (mg·L^{-1})	9.53
NO_2-N (mg·L^{-1})	20.17
COD (mg·L^{-1})	416.2
pH	8.53
TP (mg·L^{-1})	28.93
Ca (mg·L^{-1})	116
Mg (mg·L^{-1})	63
K (mg·L^{-1})	398

TKN, total Kjeldahl nitrogen; DKN, dissolved Kjeldahl nitrogen; TP, total phosphorus.

2.3. Sampling process

Before ozone aerating, the inner wall of the aeration device was cleaned and rinsed with distilled water. Then, 1 L anaerobic swine wastewater was added into the aeration device from inlet and mixed uniformly. 10 mL wastewater in device was collected at 0, 10, 20, 40 and 60 min, respectively, and labeled as t_0, t_{10}, t_{20}, t_{40} and t_{60}. Previous experiment showed that hygiene indicators, such as fecal coliform, were removed by 100% after 60 min ozone aeration.

2.4. Indicators and measuring method

Ammonium nitrogen (NH_4-N), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), dissolved Kjeldahl nitrogen (DKN), total Kjeldahl nitrogen (TKN) in the wastewater were monitored. Wastewater samples were directly digested and tested for TKN. Before testing other indicators, wastewater samples should be filtered through 0.45 μm fiber membrane in advance. In addition, TKN consists of total organic nitrogen (TON), dissolved NH_4-N [9], and particulate organic nitrogen (PON) which may be adsorbed on the surface of inorganic particles or colloid. Because the particles and colloid have limited absorption capacity and vulnerable physicochemical property, and was easily disturbed by water quality [10], PON was disregarded in the determination of water quality [11]. Other formations of nitrogen were calculated as follows [10]:

Dissolved organic nitrogen (DON) = DKN – NH_4-N

Dissolved inorganic nitrogen (DIN) = NH_4-N + NO_3-N + NO_2-N

Particulate organic nitrogen (PON) = TKN – DKN.

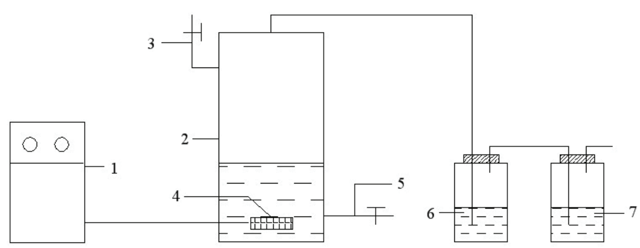

Fig. 1. Schematic diagram of ozone aeration device. (1) Ozonator, (2) aeration device, (3) inlet, (4) aerator, (5) outlet, (6) ammonia absorption solution and (7) potassium iodide-starch.

2.5. Data processing and analysis

A SAS v8.0 was adopted for data significant difference analysis, and test on the 0.05 level by Duncan's new multiple range method. Figures and table were completed in Microsoft Excel software 2010.

3. Results

3.1. NH_4-N and DKN dynamics

Effect of ozone aeration on dynamics of NH_4-N and DKN in swine wastewater is shown in Fig. 2. NH_4-N concentrations in wastewater decreased with increase in ozone aeration time, the concentrations reached significant differences levels ($p < 0.05$) at the period of t_{10}, t_{20}, t_{40} and t_{60} compared with t_0, it totally reduced by 126.10 mg/L from t_0 to t_{60}, and account for 17.90% to the initial concentration. DKN presented same characteristics with NH_4-N, the same decreased with increase in ozone aeration time, but it showed no significant differences from t_0 to t_{40}. DKN totally reduced by 47.44 mg/L ($p < 0.05$) from t_0 to t_{60}, and amount for 6.57% to the initial. Both reducing rate and concentration of NH_4-N exceeded DKN at every sampling time.

3.2. NO_3-N and NO_2-N dynamics

Fig. 3 shows NO_3-N and NO_2-N dynamics affected by ozone aeration. NO_3-N concentration increased obviously over aeration time. And NO_2-N concentration declined quickly last to be stable. NO_3-N concentration in wastewater at period from t_{10} to t_{60} had significant differences ($p < 0.05$) compared with t_0. NO_3-N concentration increased to 58.5 mg/L at t_{60}, same as increased by 613.85% than t_0. NO_2-N decreases mainly occurred in the first 10 min after ozone aeration. In this stage, NO_2-N concentration decreased by 19.42 mg/L, which occupied 97.44% of NO_2-N inversion quantity in the whole reaction process from t_0 to t_{60}. It showed NO_2-N could be oxidized quickly when ozone aerated. NO_2-N concentration in wastewater was substantially stable after first 10 min. The reduction of NO_2-N concentration in the following 50 min was only 0.51 mg/L. NO_2-N concentration at t_{60} decreased 98.81% compared with t_0. And the increment of NO_3-N concentration was larger than the decrement of NO_2-N concentration in the entire system.

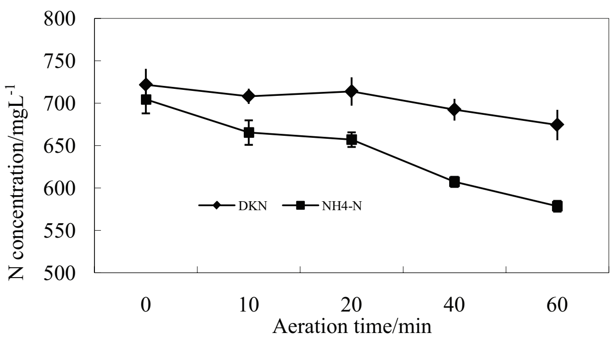

Fig. 2. Dynamics of NH_4-N and DKN in wastewater with ozone aeration.

3.3. PON and DON dynamics

Effect of ozone aeration on dynamics of PON and DON in swine wastewater is shown in Fig. 4. PON concentration in wastewater dropped sharply as aeration continued, while the concentration of DON was on the contrary. And both changing rate reduced as the aeration increases, and gradually came to a standstill. PON concentration at t_{60} decreased by 75.66 mg/L than at t_0 – reduction rate was almost 89.33%. On the other hand, DON concentration increased by 78.68 mg/L after 60 min aeration – 3.60 folds DON was produced. At t_{60}, the increase of PON was approximately equal to the decrease of DON. There were significant differences ($p < 0.05$) of PON and DON at every period of the process.

3.4. TKN and DKN dynamics

Effect of ozone aeration on dynamics of TKN and DKN in swine wastewater is showed in Fig. 5. Both TKN and DKN concentrations declined with continuation of ozone aeration. Both concentrations became close with time. This shows that PON was constantly oxidized and decomposed. Meanwhile, DKN concentration had a slightly upward trend from t_{10} to t_{20}. It was indicated that PON was oxidized and decomposed into DKN. TKN decreased by 123.09 mg/L after 60 min ozone aeration. And equivalently decrease by 15.27%. TKN concentration from t_{10} to t_{60} had significant difference ($p < 0.05$) compared with t_0.

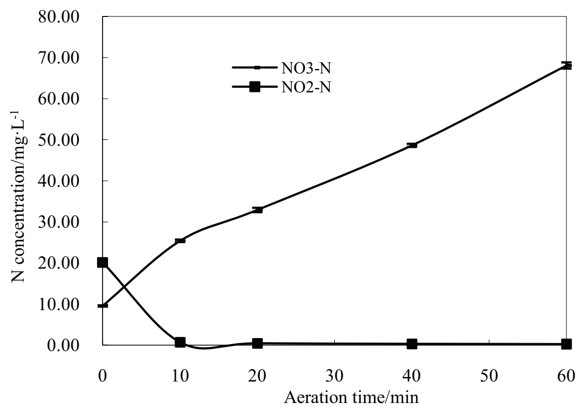

Fig. 3. Dynamics of NO_3-N and NO_2-N in wastewater with ozone aeration.

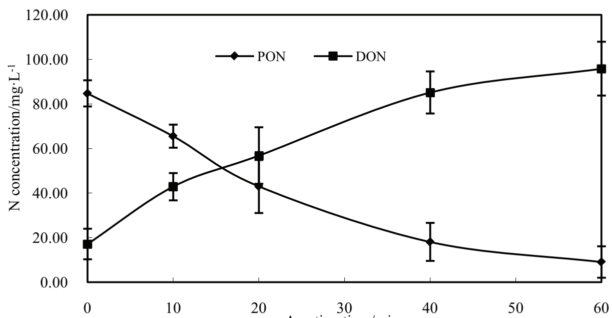

Fig. 4. Dynamics of PON and DON in wastewater with ozone aeration.

3.5. Nitrogen dynamics after ozone aeration

Nitrogen constitution and content dynamics before and after ozone aeration are shown in Fig. 6. The total amount of nitrogen at t_0 was consistent with the amount at t_{60} in wastewater system. However, the different nitrogen forms and constitutes changed significantly after ozone aeration. Gaseous ammonia volatilization lead to a loss of DON, it occupied 10.11% of TKN. While particulate nitrogen oxidized and decomposed into DON, it made a balance of DON in the whole process. After 60 min of ozone aeration, PON decreased by 89.4% and DON increased by 459.85%.

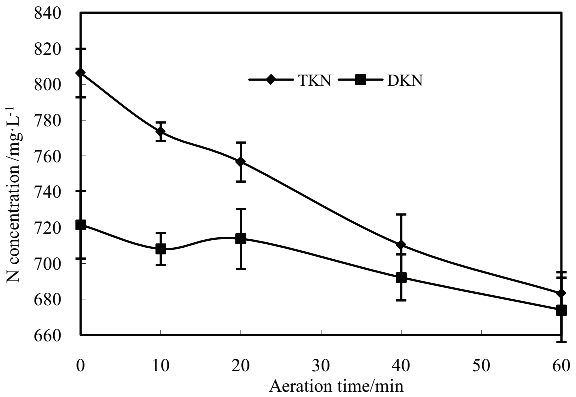

Fig. 5. Dynamics of TKN and DKN in wastewater with ozone aeration.

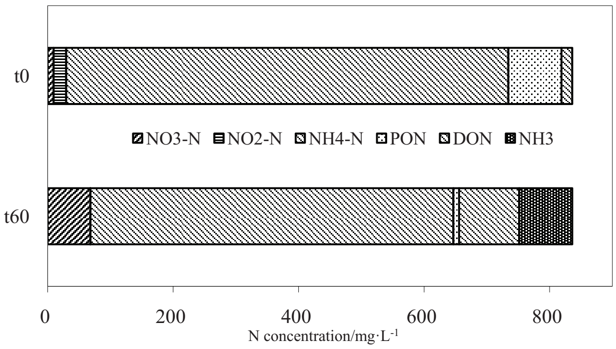

Fig. 6. Forms of nitrogen in the wastewater without and with ozone aeration.

The NO_3-N concentration at t_{60} was much higher than the sum of NO_3-N and NO_2-N at t_0. It indicated that there existed the conversion of NH_4-N to NO_3-N. NH_4-N was still the main nitrogen form in swine wastewater, though it had a significant decreasing trend. One reason is NH_4-N will be stripped by ozone and volatilized as ammonia gas, the other reason is NH_4-N will turn into NO_3-N under the strong oxidation of ozone.

3.6. Correlation analysis of nitrogen content

Correlation analysis on various forms of nitrogen content with ozone aeration is shown in Table 2. TKN had significantly positive correlation with DKN, NH_4-N and PON, and significantly negative correlation with NO_3-N and DON at the 0.01 level. DKN had significant positive correlation with NH_4-N and PON, and significantly negative correlation with NO_3-N and DON. NH_4-N had highly negative relation ($p < 0.01$) with NO_3-N and DON, and it had extremely positive relation with PON ($p < 0.01$). There was significant positive correlation at the 0.01 level between NO_3-N and DON, and significant negative correlation with PON ($p < 0.01$). PON and DON had a highly significant correlation ($p < 0.01$). Overall, NO_2-N had no significant correlation with other indexes, while there were significant or extremely significant correlations among other nitrogen indexes.

4. Discussion

As a strong oxidant, ozone can remove most microorganisms in wastewater. It is widely used in the field of water disinfection [12–16]. Swine wastewater used in the test was weakly alkaline; alkaline conditions can promote the dissociation of ozone and generate hydroxyl radicals, which has stronger oxidizing capacity compared with ozone. TKN content reduced 15.27% after 60 min of ozone aeration in this study. Tripathi et al. [17] and Beltran et al. [18] had similar results. They found that the removal rate of TN was between 15% and 32% under the different concentrations of ozone treatment. In the meantime, nitrogen was detected in boric acid absorption solution, it indicated that nitrogen volatilized in the form of ammonia nitrogen under the effect of ozone aeration. DKN and NH_4-N had the same reduction trends with ozone aeration. Nevertheless, DKN and NH_4-N (DON) were increasing with ozone aeration. It showed that

Table 2
Correlation analysis of nitrogen in different forms in swine wastewater

	TKN	DKN	NH_4-N	NO_3-N	NO_2-N	PON	DON
TKN	1						
DKN	0.9578*	1					
NH_4-N	0.9979**	0.9697**	1				
NO_3-N	–0.9928**	–0.9660**	–0.9923**	1			
NO_2-N	0.6981	0.5946	0.7100	–0.6972	1		
PON	0.9852**	0.8945*	0.9749**	–0.9692**	0.7319	1	
DON	–0.9932**	–0.9241*	–0.9894**	0.9796**	–0.7581	–0.9948**	1

*Significant correlation at 0.05 level ($n = 5$).
**Significant correlation at 0.01 level ($n = 5$).

PON continuously decomposed into soluble forms of nitrogen under strong oxidizing effect. DKN concentration was decided by two processes. One is the PON decomposition and the other is the ammonia volatilization.

Ammonium can be converted by two ways. First is ammonia volatilization. Second is ammonium nitrate oxidation. At the end of 60 min, nitrite nitrogen concentration reduced by 19.93 mg/L, while the nitrate nitrogen increased by 57.50 mg/L. The results indicated that there were 37.57 mg/L nitrate nitrogen from ammonium nitrate oxidation. It can be observed from Figs. 2 and 3 that ammonium nitrogen decreased linearly from t_{20} to t_{60}, while nitrate nitrogen increased linearly. It indicated that ammonium was partly oxidized to nitrate under ozone action. Allen et al. [19] deduced that ozone could significantly promote the ammonium nitrogen oxidation. The reference was proved by this study.

In the process of ozone aeration, PON would be decomposed constantly with the strong oxidizing effect of ozone. The decrease of PON concentration and the increase of DON concentration were same. It manifested that the TON was substantially unchanged. The nitrogen removal was mainly achieved through ammonia volatilization. Moreover, particulate nitrogen oxidation process, nitrogen form and quantity dynamics need further exploration.

5. Conclusion

The total amount of nitrogen may keep balance before and after the ozone aeration in anaerobic swine wastewater system (liquid and gas). Ammonia nitrogen volatilization loss in liquid reached 10.11% of total nitrogen when the ozone aeration. Ozone aeration had significant affect on nitrogen forms in anaerobic swine wastewater. DKN, ammonium nitrogen, nitrite nitrogen and PON were reduced with ozone aeration, and decreased by 6.75%, 17.90%, 98.81% and 89.33%, respectively, after 60 min of ozone aeration. Nitrate nitrogen and DON increased with aeration by 613.85% and 459.85% at the end of 60 min, respectively. The forms of nitrogen (except nitrite) significantly correlated with the ozone aeration process of reaction system. It also required further experimental study to verify PON oxidation process in the ozone aeration process.

Acknowledgments

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